Influence of reptations on conformations of the homopolymer in Monte Carlo simulation

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Abstract

We study the role of topological restrictions for the conformational structure of a nonphantom homopolymer chain in a lattice Monte Carlo model. In the athermal regime we find that the standard Metropolis algorithm violates the detailed balance condition if both local monomer and global reptational moves are included. However, if about 1 reptation is performed per N local moves the balance is recovered and we obtain the Flory exponent value close to $\nu = 0.588$, where N is the degree of polymerisation. We also find that the structure of the collapsed globule is different at equilibrium from that after the late stage of folding kinetics. Namely, due to reptations the end, and even more so, the penultimate monomer groups tend to be buried inside the globule core with other monomers thus being more exposed to the surface.

Keywords: homopolymer, simulation, conformation, reptation, nonphantom chain

I. INTRODUCTION

It was early recognised that topological restrictions play an important role in determining the conformation and dynamics of polymer solutions [1]. One of the most important

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topological restrictions is the integrity of chain links, which implies that different parts of the polymer chain cannot pass through each other. Unfortunately, it is rather difficult to include such restrictions to analytical theories, especially to simple mean–field ones.

Nevertheless, the effects of topological restrictions can be properly studied by computer simulation techniques [2]. One such technique developed by the authors in Ref. [3] is based on a lattice Monte Carlo model. Here the Monte Carlo updates scheme includes local monomer and reptational chain moves. The former is an attempt to move a randomly chosen monomer to a randomly chosen nearby lattice site. The latter is an attempt to move a randomly chosen end monomer to a randomly chosen lattice side near the other polymer end. It is important to emphasise that this model does not permit moves that would violate the integrity of links, i.e. the chain is strictly nonphantom. This is ensured automatically due to the particular choice of the connectivity and the excluded volume parameters.

In this paper we study how the probability of performing reptational moves affects the conformations of a single homopolymer chain at good and poor solvent conditions. In particular, we compare the globules obtained by a kinetic process and at true equilibrium. Since the kinetics of polymer collapse proceeds through formation and growth of locally collapsed clusters along the chain, with their final unification into a single globule, one may expect that after the shape optimisation stage the homopolymer globule possesses a comparatively simple topological structure [3]. Indeed, a typical coil conformation before the quench possesses a statistically small number of entanglements, or knots, and the folding kinetics adds virtually nothing to that number. Further relaxation of the globule towards the equilibrium requires participation of the chain ends and, thus, can be viewed as an auto–reptational stage. This auto–reptation time can be estimated as, $\tau_{rept} = \tau_0 N^3$ [4], which can yield a time of order 10^3 sec under usual experimental conditions [5].

II. THE GOOD SOLVENT REGIME

In this section we shall test the Monte Carlo scheme by determining the value of the swelling exponent ν [1], in the good solvent regime.

Generally, it seems that to improve the convergence of the system to equilibrium various types of global moves, such as reptations, may be included in addition to local ones. The resulting equilibrium state should not depend on a particular scheme involved. To test this assumption let us study how the probability of performing reptations, p_r, affects the value of the Flory exponent of the coil. The results are presented in Tab. I. One can see that the value of ν obtained in the scheme without reptations (at the bottom of the left column) is somewhat higher than even the mean–field prediction $\nu = 3/5$. As we increase the probability of performing reptations ν starts to decrease. In the limit when only reptations are performed, $p_r = 1$, the swelling exponent value is found to be 0.56. Note that for the probability $p_r = 1/N$ the measured swelling exponent is remarkably close to the most accurate result obtained from the renormalisation group theory, $\nu \approx 0.588$ [1].

We may conclude therefore that the scheme with only reptations involved leads to more compact entangled conformations, resulting in underestimation of the swelling exponent. On the other hand, the scheme with local monomer moves only favours topologically simple conformations as it is rather improbable to create a knot by local movements. If some knots already exist in the initial conformation, the local monomer movements would tend to disentangle them. Indeed, one can imagine that simple 'shaking' of an entangled boot strap would more likely disentangle it rather than entangle it more. This weak topological effect reduces the number of entanglements, which leads to a larger radius of gyration and overestimation of the swelling exponent in the scheme with local moves only.

Such strong dependence on the reptation probability p_r is quite unexpected from the point of view of the standard Monte Carlo paradigm. Of course, the Metropolis check in itself is not sufficient for satisfying the detailed balance condition. One also has to ensure the condition that the phase space of the system is sampled uniformly by attempted Monte Carlo moves [6] (see Appendix for more detail). Although, this may be quite simple to ensure for point–like objects, in our case of a nonphantom chain this is not so. The above observations do indicate clearly that the current sampling procedure is not uniform, but biased. The bias is present in both schemes with reptations only and local moves only, but has the opposite effect. We have also seen that if about 1 reptation is performed per N

Monte Carlo steps the topological effects of entanglements and disentanglements balance each other, making the sampling of the phase space essentially uniform and producing the correct swelling exponent.

However, we should emphasise that this problem of the improper influence of reptations is only present for the Flory coil and it is irrelevant for the ideal coil. Both schemes with local moves only and reptations only would give $\nu = 1/2$ for the ideal solution. That is why reptation techniques are extremely popular and well justified for studying melts and concentrated solutions, in which reptations also may be the only physically relevant motions. We should also emphasise that if the chain was phantom we would not have this problem either.

Even though the above discussed effect for the Flory coil is clearly of topological origin, it only presents a problem for the simulation procedure and has no implications for real polymers.

III. STRUCTURE OF THE HOMOPOLYMER GLOBULE

In this section we shall study the structural differences between the two globules of an open homopolymer: one with a relatively simple topological structure corresponding to the late stage of folding kinetics, and another with topological entanglements. In practice these simulations have been carried out in the following way. Using the lattice Monte Carlo method a large set of homopolymer globules was produced by independent kinetic processes starting from initial coil conformations. Reptational moves were not included during this simulation. To produce true equilibrium distribution for the globule an additional simulation was applied to the set with amount of reptational moves equal to $p_r = 1/N$.

Let us introduce the mean squared distances along the chain, D_{mn}, and their partially summated combinations, D_k

$$D_{mn} = \left\langle (\mathbf{X}_m - \mathbf{X}_n)^2 \right\rangle, \qquad D_k \equiv \frac{1}{N-k} \sum_{i=0}^{N-1-k} D_{i\,i+k}. \tag{1}$$

In Fig. 1 we present the quantity $D_{\hat{k}}$ versus the normalised chain index, $\hat{k}$, for polymers of different degrees of polymerisation. For very small chain indices function D_k does not depend

on N and on the particular simulation procedure, which reflects local packing of monomers in the dense globule. Let us consider first the behaviour of this function for globules prepared without reptations. For small values of the chain index the function is almost linear, up to some cross–over value that scales as $N^{2/3}$. Then it saturates to some level, which is proportional to the radius of the globule, thus also scaling as $N^{2/3}$. Interestingly enough, for values of the chain index in the vicinity of the chain ends the function D_k increases once again. This phenomenon actually reflects the mechanism of the polymer collapse during late coarsening stage. The globule is usually formed by a final unification of two end clusters and, sometimes, a few middle clusters (see e. g. Figs. 4, 6 and 10 in Ref. [3]). Thus, the chain ends possess a somewhat higher probability to appear on opposite sides of the globule than the rest of monomers. This effect in the mean squared distances is fairly weak as the function experiences about 10% increase towards the ends.

In fact, this observation is related to the observation that the chain ends are more exposed to the globule surface, and it can be better justified by considering the probability of the m-th monomer in the chain to appear on the surface of the globule, $P_m^{(surf)}$. This is presented in the left–hand–side part of Fig. 2. Thus, the function $P_m^{(surf)}$ for kinetic simulation is nearly constant except for a few monomers at the very chain ends. In particular, for the end monomer this probability is about 1.3 times larger than that for a monomer in the centre of the chain.

The effect due to applying reptational moves during later kinetic stages is quite distinguishable in observables in Figs. 1 and 2. For sufficiently large values of the chain indices, $\hat{k} \gtrsim 0.35 - 0.4$, the function of mean squared distances obtained from simulation with reptations (see lines denoted by diamonds in Fig. 1) lies below the appropriate curves from the kinetic simulation. The situation is just the reverse for smaller k, with the difference slowly vanishing towards $k = 0$. Thus, the reptational curve for D_k behaves in the following way: it is linear for small k, reaches a maximum at around $\hat{k} = 0.3$ and then slowly decreases reaching a minimum in the vicinity of the chain ends. At the very end the function increases strongly, still being significantly smaller that for the function D_k without reptations.

Note that the partially summated mean squared distances are not fully informative due to

the role of the end effects in an open chain. Thus, let us consider the mean squared distances as functions of two indices. In Fig. 3 we exhibit the ratios of mean squared distances with and without reptations, $D^{(r)}_{mn}/D^{(n)}_{mn}$. Depending on the behaviour of this ratio, the monomers in the chain may be roughly divided into three groups: for monomers in the centre of the chain, $0.1 \lesssim m/N \lesssim 0.9$, the mean squared distances significantly increase due to reptations; for groups of penultimate to the end monomers, $3 \lesssim m$, $N - m - 1 \lesssim 0.1N$, the distances decrease due to reptations, with the effect becoming more pronounced on approaching the ends of the chain; and for a few end monomers the distances decrease but much more weakly. Thus, we can conclude that reptations push the end groups somewhat and the penultimate groups of monomers more so towards the centre of the globule, thus reducing their mean squared distances between each other and monomers from the central group. As the density of the globule does not change here this leads to an increase of the mean squared distances for monomers in the centre of the chain.

Such behaviour of the mean squared distances is quite consistent with the plot of the surface probability $P^{(surf)}_m$ after reptational stage (right–hand–side of Fig. 2). This quantity increases for monomers in the central group by about 10% and, instead of being constant, decreases slowly towards the ends of the chain. The drop in the probability is most pronounced for monomers from the penultimate groups. The function rapidly increases for a few monomers at the very ends of the chain, although, they still possess a lower probability to be found on the surface than monomers from the central group. This rapid increase of the probability for a few end monomers may be interpreted as an effect of a single end seeking to maximise its entropy. Indeed, the chain ends are most free to explore the surface, whilst the rest of monomers are more restricted due to connectivity.

IV. CONCLUSION

In this paper we have applied the lattice Monte Carlo model of Ref. [3] to study the role of reptations for conformations of the nonphantom homopolymer chain.

First, we have considered the athermal good solvent regime and discovered that the fre-

quency of performing reptations significantly affects the size and even the swelling exponent of the polymer. This problem arises due to a nonuniform sampling of the phase space of the system by attempted Monte Carlo moves. For a nonphantom chain it is not clear how to ensure uniform sampling especially between conformations with different topological numbers. The scheme with reptations only is biased towards entangled conformations, while the scheme with local moves only samples topologically simple states more. However, the balance is recovered when the probability of reptations is equal to $p_r = 1/N$.

Second, we have compared structures of the two globules: one corresponding to late stages of kinetics and another to the true equilibrium. The globule after the late kinetic stage is characterised by a uniform monomer distribution except for the end monomers, which have a higher probability to be on the surface. Due to reptations the end, and even more so, the penultimate monomer groups are pushed more towards the centre of the globule, with the central monomer group thus being more exposed to the surface. A typical magnitude of this effect in observables expressing the k-dependent properties is about a few dozens percents in the relative change, while the global characteristics such as the mean energy and radius of gyration are practically unaffected by this conformational change. The latter is a physically important conclusion for real polymers.

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APPENDIX: THE PROBLEM OF UNIFORM SAMPLING IN THE METROPOLIS ALGORITHM

The system is simulated based on the Metropolis algorithm [2] for calculation of the statistical averages in the system at temperature T.

Its main idea is to construct a Markov process in the phase space,

$$\mathbf{X}_A(1) \to \mathbf{X}_A(2) \to \ldots \to \mathbf{X}_A(i-1) \to \mathbf{X}_A(i) \to \ldots, \tag{A1}$$

where each state $\mathbf{X}_A(i)$ follows from the previous one $\mathbf{X}_A(i-1)$ according to the transition probability, $\Pi(\mathbf{X}'_A \to \mathbf{X}_A)$.

Let $P_0(\boldsymbol{X}_A)$ denotes the initial probability with any distribution, e.g. uniform. At each time step we update these probabilities by a certain rule. The updated probabilities set may be obtained as, $P_1(\boldsymbol{X}_A) = \sum_{\boldsymbol{X}'_A} \Pi(\boldsymbol{X}'_A \to \boldsymbol{X}_A)\, P_0(\boldsymbol{X}'_A)$, where $\Pi(\boldsymbol{X}'_A \to \boldsymbol{X}_A)$ is the corresponding transition probability. We then repeat the above procedure many times using the results from the previous step as input.

Let us introduce the *balance condition*, which expresses the stationarity of the equilibrium distribution, $P_{eq}(\mathbf{X}_A) = Z^{-1} \exp(-\beta H(\mathbf{X}_A))$, with respect to the action of the Markov process:

$$P_{eq}(\mathbf{X}_A) = \sum_{\mathbf{X}'_A} \Pi(\mathbf{X}'_A \to \mathbf{X}_A)\, P_{eq}(\mathbf{X}'_{A'}). \tag{A2}$$

Next, the *ergodicity condition* means that the phase space does not factorise into disjoint parts, i.e. for any $\mathbf{X}'_A$ and $\mathbf{X}_A$ there exists a finite sequence of $\mathbf{X}_A(i)$ $i = 1, \ldots, m$ such that $\Pi(\mathbf{X}'_A \to \mathbf{X}_A) \neq 0$ and $\mathbf{X}_A(1) = \mathbf{X}'_A$ an $\mathbf{X}_A(m+1) = \mathbf{X}_A$. In other words, the system can go from any state to any other state by a finite number of steps.

These two conditions are sufficient for convergence of the ensemble produced by a Markov process to the equilibrium distribution [6]. To show that we need to introduce the notion of the "distance" between two ensembles E and E' via the norm [6],

$$||E - E'|| = \sum_{\mathbf{X}_A} |P(\mathbf{X}_A) - P'(\mathbf{X}_A)|. \tag{A3}$$

Now, if the ensemble E' is obtained from E by action of one step in the Markov chain we have,

$$P'(\mathbf{X}_A) = \sum_{\mathbf{X}'_A} \Pi(\mathbf{X}'_A \to \mathbf{X}_A)\, P(\mathbf{X}'_A). \tag{A4}$$

This allows us to obtain the following estimate,

$$||E' - E_{eq}|| = \sum_{\mathbf{X}_A} \left| \sum_{\mathbf{X}'_A} \Pi(\mathbf{X}'_A \to \mathbf{X}_A)(P(\mathbf{X}'_A) - P_{eq}(\mathbf{X}'_A)) \right| \tag{A5}$$
$$\leq \sum_{\mathbf{X}_A, \mathbf{X}'_A} \Pi(\mathbf{X}'_A \to \mathbf{X}_A) \, |P(\mathbf{X}'_A) - P_{eq}(\mathbf{X}'_A)| = ||E - E_{eq}||,$$

where we have used the non–negativeness of the transition probability and the normalisation condition, $\sum_{\mathbf{X}'_A} \Pi(\mathbf{X}'_A \to \mathbf{X}_A) = 1$. Thus, application of such a step moves the ensemble closer to the equilibrium. Finally, note that the inequality in Eq. (A5) becomes strict thanks to the ergodicity, and so the equality is only possible when the ensemble has reached the equilibrium.

Instead of the balance condition (A2) one can apply a more restrictive *detailed balance condition*, which relates the transition probabilities of the forward and backward transitions,

$$\exp\left(-\frac{H[\mathbf{X}_A]}{k_B T}\right) \Pi(\mathbf{X}_A \to \mathbf{X}'_A) = \exp\left(-\frac{H[\mathbf{X}'_A]}{k_B T}\right) \Pi(\mathbf{X}'_A \to \mathbf{X}_A), \tag{A6}$$

which obviously produces the latter balance condition by summing over $\mathbf{X}'_A$.

In the Metropolis algorithm one step of the Markov chain is generated in two steps:
1. Given $\mathbf{X}_A(n)$ one generates a trial conformation $\mathbf{X}_A(T)$ by a random algorithm with a symmetric transition probability,

$$\Pi_S(\mathbf{X}_A(n) \to \mathbf{X}_A(T)) = \Pi_S(\mathbf{X}_A(T) \to \mathbf{X}_A(n)). \tag{A7}$$

This process looks like a simple random walk in the phase space and does not depend on the particular Hamiltonian H of the system. For instance, for the Ising model it would mean to pick up a randomly chosen spin.
2. Perform a transition with the conditional probability $\Pi_M(\mathbf{X}_A(n) \to \mathbf{X}_A(T))$, so that the total transitional probability is,

$$\Pi(\mathbf{X}_A(n) \to \mathbf{X}_A(T)) = \Pi_S(\mathbf{X}_A(n) \to \mathbf{X}_A(T)) \, \Pi_M(\mathbf{X}_A(n) \to \mathbf{X}_A(T)). \tag{A8}$$

A simple choice of this transition probability was proposed by Metropolis et al,

$$\Pi_M(\mathbf{X}_A \to \mathbf{X}'_A) = \begin{cases} \exp\left(-\frac{\Delta H}{k_B T}\right), & \text{for } \Delta H \equiv H[\mathbf{X}'_A] - H[\mathbf{X}_A] > 0, \\ 1, & \text{for } \Delta H \leq 0. \end{cases} \tag{A9}$$

Due to the explicit definition of Π_M and symmetricity of the matrix Π_S the total transition probability Π still satisfies the detailed balance condition.

Thus, despite many popular beliefs, the Metropolis check itself is not sufficient for satisfying the detailed balance condition. We also have to ensure the condition that the phase space of the system is sampled uniformly by attempted Monte Carlo moves, so that the transition probability $\Pi_S(old \to new)$ is symmetric. This may be simple enough to ensure for point–like objects by simply picking them at random, however, in our case of a nonphantom polymer chain this is not quite so easy due to the topology.

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TABLES

TABLE I. Values of the mean squared radius of gyration, R_g^2, vs the degree of polymerisation, N, for different simulation procedures. Here Q is the number of statistical measurements, p_r is the probability of making reptations in the scheme, with $1 - p_r$ being the probability of making local monomer moves. The exponents ν_1 and ν_2 were obtained by a least square fit of $\log R_g$ vs $\log N$ in the ranges $100 - 1000$ and $500 - 1000$ respectively.

N	$p_r = 0$	$p_r = 1/N$	$p_r = 0.1$	$p_r = 1$
Q	80,000	60,000	40,000	40,000
20	13.14	12.55	12.29	11.50
30	22.21	20.74	19.88	18.44
50	42.16	38.50	35.73	32.63
70	64.89	57.66	52.54	48.45
100	98.17	88.15	77.75	72.54
150	162.2	142.7	122.6	112.9
200	227.2	201.2	169.0	156.8
300	381.2	322.7	261.8	245.9
500	696.5	588.1	460.0	435.9
700	1029	856.1	667.2	637.6
1000	1643	1329	991.5	947.7
ν_1	0.608	0.587	0.551	0.559
ν_2	0.619	0.588	0.554	0.560

FIGURES

FIG. 1. Plot of the partially summated mean squared distances, $D_{\hat{k}}$, vs the normalised chain index, $\hat{k} = k/(N-1)$, for homopolymer globules of different sizes and different simulation procedures. Pairs of lines correspond respectively to the following values of the degree of polymerisation (from bottom to top): $N = 50$, $N = 100$ and $N = 200$. Lines denoted by diamonds and pluses in each pair correspond to the simulation procedures with, $p_r = 1/N$, and without reptations, $p_r = 0$, respectively.

FIG. 2. Plot of the probability, $P_m^{(surf)}$, for the m-th monomer in the chain to appear on the globule surface vs the monomer index, m, for the homopolymer with the degree of polymerisation, $N = 400$, for different simulation procedures. The left– and right–hand–side curves correspond to the kinetic (no reptations) and reptational simulation procedures. Both distributions are symmetric in monomer index, m, and for convenience they are presented only on halves of the interval.

FIG. 3. Diagrams of the ratios of the mean squared distances with and without reptations, $D_{mn}^{(r)}/D_{mn}^{(n)}$ for different values of the degree of polymerisation. Diagrams (a) and (b) correspond respectively to the following values of the degree of polymerisation: $N = 100$ and $N = 200$. Indices m, n start counting from the upper left corner. Each matrix element is denoted by a quadratic cell with varying degree of black colour, the darkest and the lightest cells corresponding respectively to the smallest and to the largest ratios of the mean squared distances. Intensity of black colour in the near diagonal elements corresponds approximately to the ratio $D_{mn}^{(r)}/D_{mn}^{(n)} = 1$.

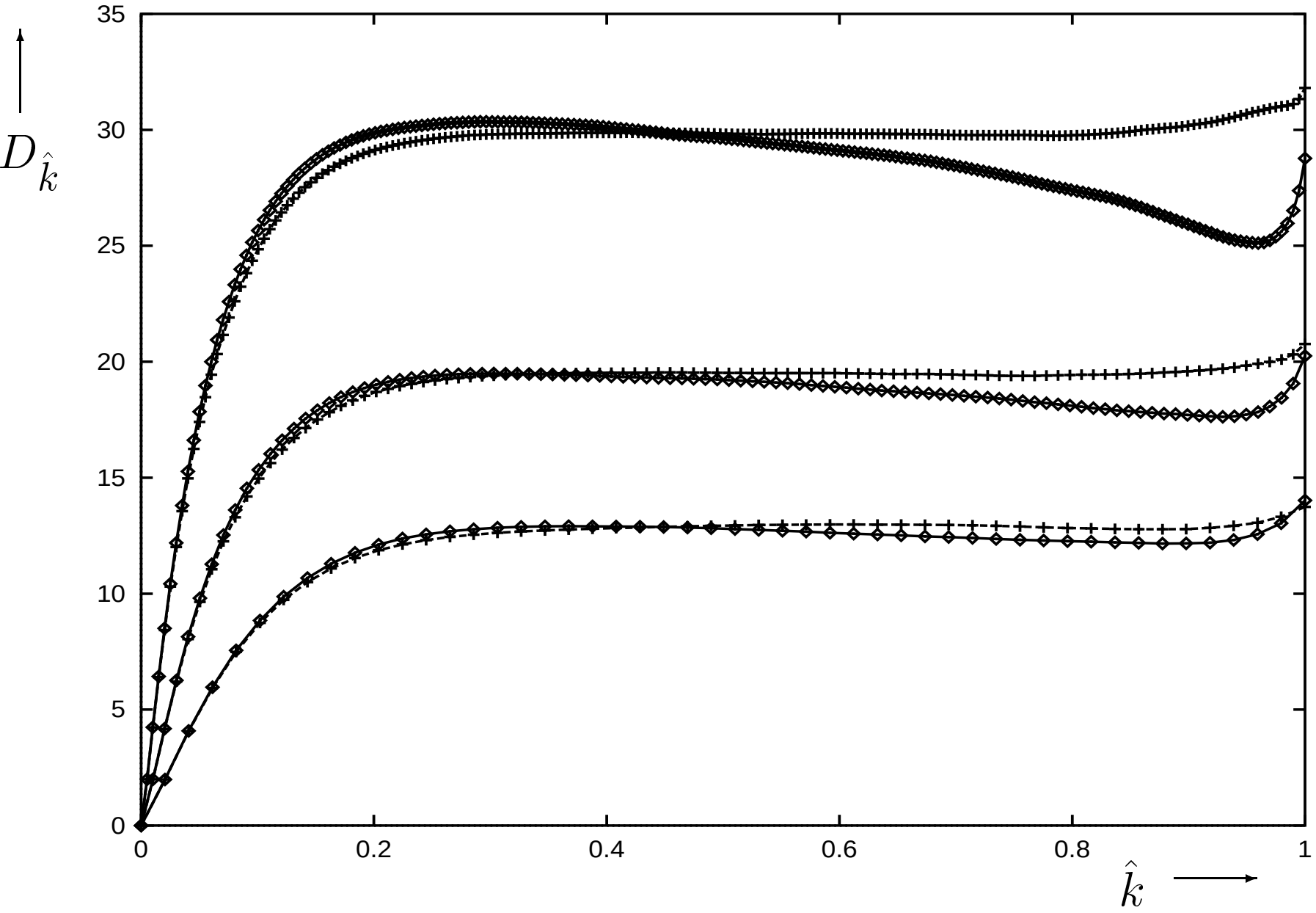


Fig. 1

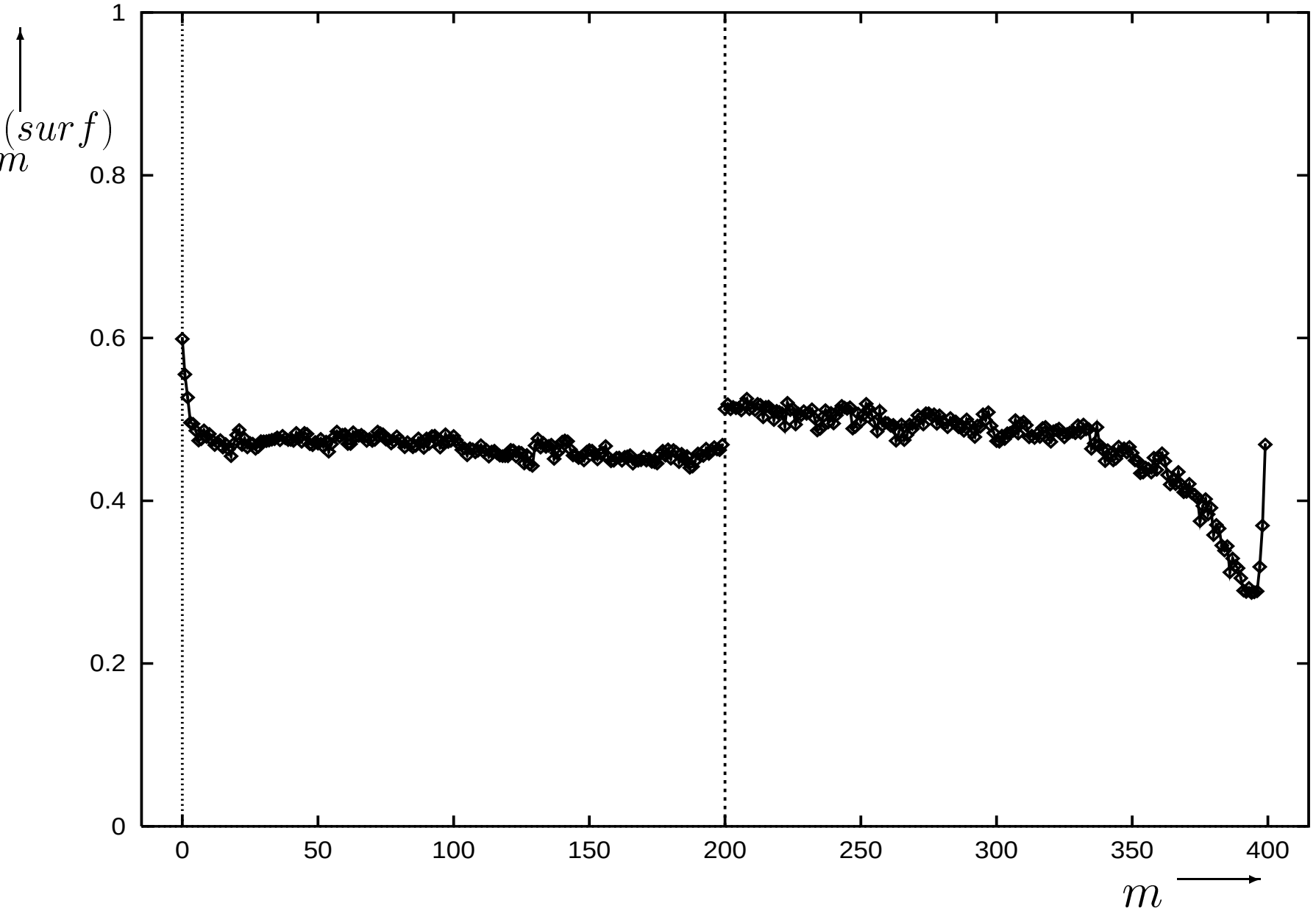
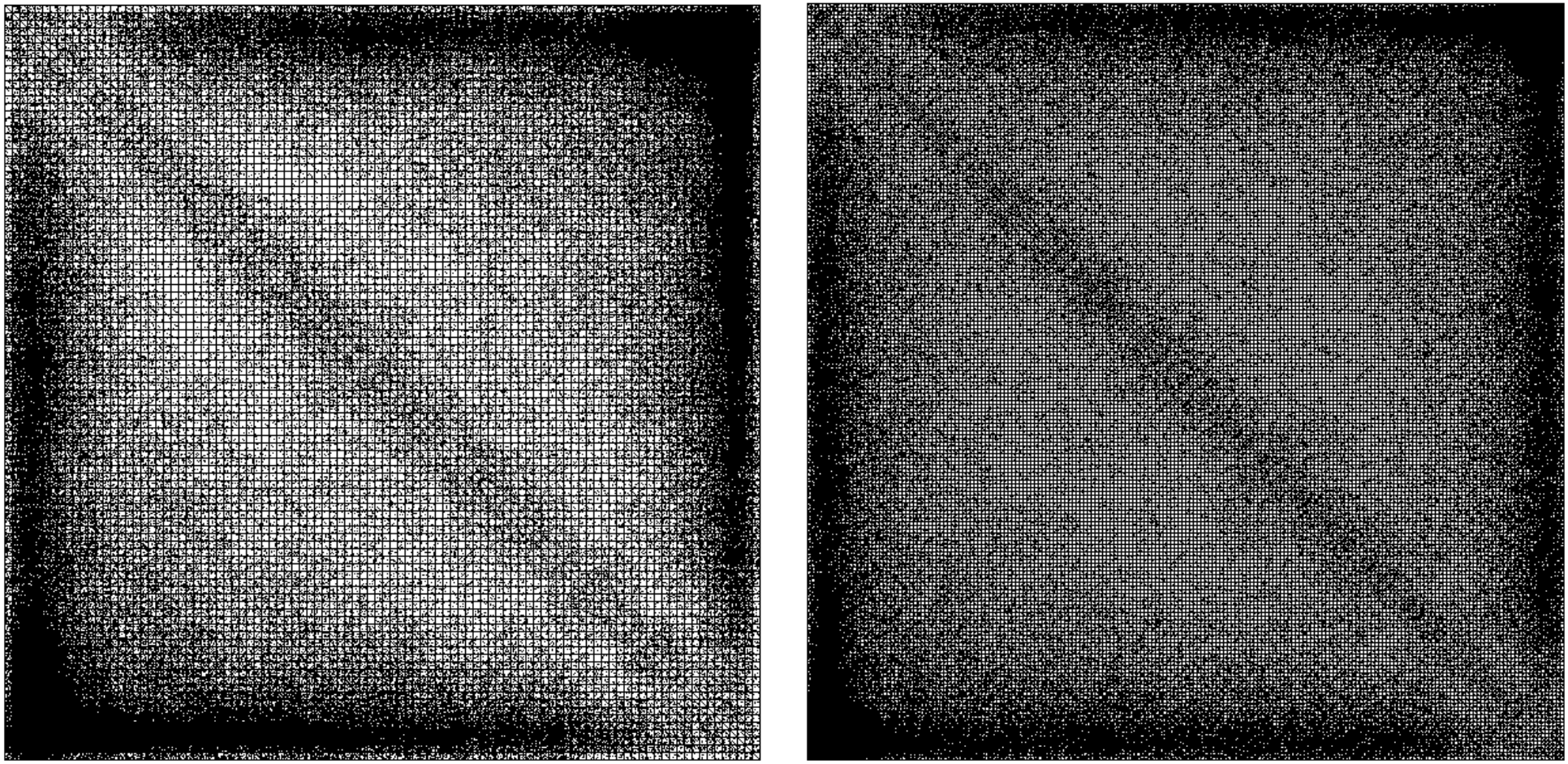


Fig. 2



(a) (b)

Fig. 3